**GEORGIA INSTITUTE OF TECHNOLOGY**
**OFFICE OF CONTRACT ADMINISTRATION**
**SPONSORED PROJECT INITIATION**

Date: 3/10/81

Project Title: Scientific Services Program - STAS - Visible Chemical Laser Data Base

Project No: G-33-676

Project Director: Dr. J.L. Gole

Sponsor: Battelle Columbus Laboratories, Durham Operations; Research Triangle Park, N.C. 27709

Agreement Period: From 3/1/81 Until ~~8/31/81~~ 7/30/81 (Perf.); ~~10/31/81~~ 11-30-81 (Rpts.

Type Agreement: Delivery Order No. 1787 (Time & Materials Subcontract under ARO Prime Contract No. DAAG29-76-D-0100

Amount: $47,040

Reports Required: Oral Reports as requested; Final Report

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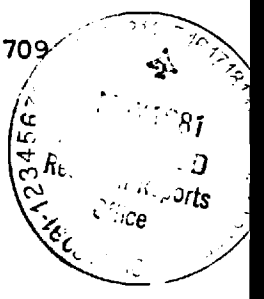

Defense Priority Rating: None

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GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

# SPONSORED PROJECT TERMINATION SHEET

Date 11/6/81

**Project Title:** Scientific Services Program - STAS - Visible Chemical Laser Data Base

**Project No:** G-33-676

**Project Director:** Dr. J. L. Gole

**Sponsor:** Battelle Columbus Laboratories, Durham Operations; Research Triangle Park, N.C. 27709

**Effective Termination Date:** 9/30/81 (Perf.)

**Clearance of Accounting Charges:** 11/30/81 (Rpts.)

**Grant/Contract Closeout Actions Remaining:**

- [X] ~~Final Invoice and~~ Closing Documents
- [ ] Final Fiscal Report
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**Assigned to:** Chemistry (School/~~Laboratory~~)

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FORM OCA 10:781

Final Report
to the
SCIENTIFIC SERVICES PROGRAM
for research in support of a
VISIBLE CHEMICAL LASER DATA BASE

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PRINCIPAL INVESTIGATOR AND SENIOR SCIENTIST

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Objectives:

The purpose of this program has been to ascertain potential laser candidates and aid in the development of a visible chemical laser data base. This program has also acted in support of the research effort of Drs. John Raymonda and Gary Myers at the Bell Aerospace Corporation.

Summary of Major Research Thrusts:

The six month research program has been divided into four main areas:

(1) Efforts to develop cavity diagnostics for potential chemical laser candidates SnO (tin oxide) and YF (yttrium fluoride) using an exploding wire laser system.

(2) The investigation of ultrafast energy transfer in several systems of potential utility in an attempt to assess the feasibility for creating a population inversion through rapid E-E (electronic to electronic) or V-E energy transfer.

(3) The assessment of selective chemical reactions and the nature of the quenching of fluorescence from excited electronic states produced selectively in a chemiluminescent reaction.

(4) The formulation of theories to (a) explain selective excited state formation and (b) model the nature of those phenomena and properties which lead to ultrafast energy transfer.

Description of Specific Research Projects:

a. "Exploding Wire Laser Studies"

1. $SnO a^3\Sigma^+$

The reaction of tin atoms and $N_2O$ at pressures on the order of one torr is thought to produce electronically excited tin oxide (SnO*) with

high quantum yield[1] in a relatively long-lived $^3\Sigma^+$ state. It is thought that lasing action might be initiated on the $a^3\Sigma^+ - X^1\Sigma^+$ band system, specifically on the (0,2), (0,3), or (0,4) transitions at ~5307Å, ~5532Å, or ~5799Å. Using and exploding wire laser system on loan from Los Alamos Scientific Laboratory, we have been evaluating the best conditions ($N_2O$ and background gas pressure (He and Ar)) under which one might achieve the requisite lasing in SnO. We believe that these experiments are meeting with good success and that conditions have been established which look close to optimal for $N_2O$/He and $N_2O$/Ar mixtures. Further, we have studied the $NO_2$/He system which also yields SnO $a^3\Sigma^+$. Some typical studies are indicated in Figures 1-4. Several factors in systems operation are indicated in these figures which were obtained using a back high reflector but no output coupler in the cavity. Figure 1 demonstrates the difference between two runs under similar pressure and detection conditions for helium and argon. Here a tin wire is exploded into a mixture of $N_2O$ and helium or $N_2O$ and argon. Figure 2 shows the spectra obtained for an argon based system with and without $N_2O$ demonstrating that three atomic transitions for $Sn^+$ are virtually in coincidence with the 5532Å SnO band (two $Sn^+$ lines) and the 5799Å SnO band (one line). This is further demonstrated in Figure 3 for $N_2O$/He mixtures and lends credence to the possibility of a laser based on $SnO^*(a^3\Sigma^+) + Sn^+ \rightarrow Sn^{+*} + SnO$ electronic to electronic energy transfer. Of course additional studies have been carried out over a wide range of $N_2O$ and buffer gas pressures.

Further explanation of the spectra in Figures 2 and 3 is in order. All of these scans were taken using Panatonic ASA25 film. The spectra in Figure 3 correspond to tin oxide (SnO) features on which are superimposed $Sn^+$ and Sn atomic lines. As the $N_2O$ pressure is increased, the underlying SnO features increase in intensity and the $Sn^+$ atomic features broaden and are skewed to longer wavelength. In contrast, the Sn atomic line at 5631Å is virtually unaffected.

Figures 2 and 3 in combination demonstrate that the broadening of the $Sn^+$ lines is a pressure induced as opposed to electric field induced phenomena. Further studies demonstrate that the skewed broadening of the $Sn^+$ lines is due to $Sn^+$-$N_2O$ or $Sn^+$-$N_2$ interaction, the latter interaction becoming a factor at higher ($\geq$40 torr) $N_2O$ cavity pressures. $N_2$ is produced in the exploding wire cavity via $N_2O$ dissociation during the wire explosion cycle and as a result of $N_2O$ reaction to form the metal oxide. Finally, we should note that the Panatonic film used in the initial phases of the work effort is of such a speed so as to accentuate the intensity of the $Sn^+$ emission features relative to those for SnO. Using faster Tri-X film which is 400ASA, we obtain the spectra shown in Figures 4(a) and (b) for the tin-$NO_2$ system. Here, a tin wire is exploded in a mixture of five torr $NO_2$ and twenty torr helium. A comparison with the results obtained using the Tri-X and Panatonic films indicates that the $Sn^+$ emission features probably correspond to a longer-lived excited state than that of $a^3\Sigma^+$ tin oxide. At higher pressures, these $Sn^+$ features are quenched relative to the tin oxide $a^3\Sigma^+ - X^1\Sigma^+$ band system.

A great deal of the information obtained in our laboratory has been communicated to the Bell Aerospace group and a great deal of mutual insight has been gained as a result of our verbal discussions with Drs. Raymonda and Myers. Briefly, it now appears that there are subtle playoffs between the use of helium or argon as buffer gases in these systems. The studies involving $N_2O$ and argon have been run for $N_2O$/Ar ratios ranging from 5/80 to 60/20 (torr). In all cases (Figure 1) there appear to be two broad underlying continuum-like features which cover the range 3500 to 4500 and 5000-6200Å. A number of experiments indicate that these features can be attributed to polyatomic species which result from the oxidation of tin clusters produced in the exploding wire plasma. These background continua are much weaker, if non-existent, for spectra taken at low helium pressures (see Figure 1), prompting one to

believe that helium might be a better (cleaner) buffer gas than argon. However, Figure 1 also indicates that argon may well be a more efficient buffer gas for the collisional population of the $a^3\Sigma^+$ state of tin oxide. This is significant for it is thought that the $a^3\Sigma^+$ state is populated via collisional transfer from a longer-lived reservoir state.[2]

The overall data base seems to indicate that the optimum system operating conditions are in the range 10–15 torr $N_2O$, 20–40 torr argon. For helium, optimum operating conditions appear to be at somewhat higher $N_2O$ (20–30 torr) and notably higher helium ($40^+$ torr) pressures. The $NO_2$/He system operates best at 5–15 torr $NO_2$, $30^+$ torr helium. There are subtle behavior patterns which need some further fine tuning; however, clear factors are beginning to emerge. It will also be appropriate to characterize these systems with even faster film detection. For this effort, we are now assessing the value of 1600 ASA film and its relative detection limits.

We have also attempted preliminary full cavity experiments meeting with only marginal success in producing desired output at ~5307Å, ~5532, and ~5799Å. We are currently optimizing the system further, so as to carry out both spectral and temporal measurements with a full cavity. In view of the data exemplified in Figures 1–4, we envision that two possible modes of laser action might be made to occur. The first involves direct lasing on the (0,2), (0,3), or (0,4) SnO $a^3\Sigma - X^1\Sigma^+$ transitions. The second may take advantage of a very unusual situation, namely the near coincidence of SnO and $Sn^+$ features. If a highly efficient collisional transfer can be made to occur, lasing might occur on a $Sn^+$ transition. We are assessing this possibility at present.

2. YF $^3\Sigma^+$

We are proceeding with further studies of the chemiluminescence from the $Y + F_2$ system where it appears that we have observed selective formation of a relatively long-lived YF excited electronic state. This $^3\Sigma^+$ state appears to

be formed in high quantum yield and the activation energy for excited state formation is negligible. Our chemiluminescent studies have now been extended to the exploding wire laser system. Here, we find that the intensity output from the exploding wire laser cavity far exceeds that from the Sn-$N_2O$ system; however, thusfar the Y + $F_2$ system appears to be producing a great deal more atomic emission than we had hoped for on the basis of previous studies. This may, however be an artifact of our detection system. Further optimization should remedy the problem. In this regard, our careful characterization of the Sn-$N_2O$ and Sn-$NO_2$ systems should prove invaluable as a means of defining the important parameters in the Y-$F_2$ system. We anticipate returning to the T-$F_2$ system shortly or at least after completing the requisite studies on SnO.

b. "Ultrafast Energy Transfer"

The focus of this work has been on the investigation of ultrafast energy transfer among the electronic states of small high temperature molecules and the potential implications which this transfer has for the creation of population inversions on a given electronic transition. Here, we have studied fast energy transfer in boron oxide (BO), yttrium oxide (YO) and silicon oxide (SiO) with primary emphasis on BO.

In the boron oxide system there are two potentially important regions. First, there is a strong coupling between the 17th vibrational level ($v''=17$) of the ground electronic state and the fourth vibrational level ($v' = 4$) of a low-lying $A^2\Pi$ state (see Figure 5). This facilitates rapid V-E energy transfer from the ground electronic state producing a significant population in BO, $A^2\Pi$, $v' = 4$. Second, the $X^2\Sigma^+$ ground electronic

state and the $A^2\Pi$ state cross between v' = 8 and 9, $A^2\Pi$ (see Figure 5) facilitating a potential bottleneck storage region in an excited electronic state.

The nature of the BO $X^2\Sigma^+$, v'' = 17 → BO $A^2\Pi$, v' = 4 ultrafast energy transfer had been observed before this project began for BO-$O_2$ and BO-$N_2O$ collisions. We have now demonstrated that it is much more efficient for BO-$NO_2$ collisions producing a significant population in BO $A^2\Pi$, v' = 4. Sample spectra for the boron-$NO_2$ system are shown in Figures 6(a) and (b). The cross section for the B + $NO_2$ → BO* + NO reaction significantly exceeds those for B + $O_2$ → BO* + O and B + $N_2O$ → BO* + $N_2$. Note the strong emission in the region of the BO $A^2\Pi$ - $X^2\Sigma^+$ (4,0) band signalling the rapid energy transfer indicated above. Note also the sharp dropoff of spectral intensity for $A^2\Pi$ levels v' > 8. The effect observed here is a manifestation of the potential curve crossing indicated above and in Figure 5.

For the BO-$NO_2$ system, a preliminary quantitative measurement of the rate of energy transfer BO $X^2\Sigma^+$, v'' = 17 → BO, $A^2\Pi$, v' = 4 indicates a cross section well in excess of 4000Å.[2] We now have extensive single collision spectra (low pressure studies) which demonstrate our ability to populate levels beyond the crossing point of the BO $A^2\Pi$ and $X^2\Sigma^+$ states. Our efforts have concentrated on the B + $NO_2$ → BO* + NO system thusfar; however, preliminary data on the boron-ozone system indicates a very similar behavior to that demonstrated in Figures 6 and 7 for the B-$NO_2$ metathesis. The boron-ozone reaction is characterized by a sharp dropoff in BO $A^2\Pi$ - $X^2\Sigma^+$ spectral intensity for levels v' > 8 and spectral emission is observed from levels to v' = 17. Based strictly on reaction exoergicity the B-$NO_2$ and B-$O_3$ reactions might be expected to populate up to 19 and 40 levels in BO $A^2\Pi$ respectively. The effect of the BO $A^2\Pi$ - $X^2\Sigma^+$ curve crossing (Figure 5) is therefore quite dramatic. Using the

$B-NO_2$, $B-O_3$, and possibly $B-N_2O$ systems, we hope to see if a population buildup can be made to occur in the region of the $A^2\Pi - X^2\Sigma^+$ crossing point via relaxation of higher levels into a "bottleneck" region. With this in mind, we have conducted higher pressure multiple collision studies which have thusfar been marginally successful. There have been some problems with recently obtained heating elements, however, it is anticipated that these can be corrected shortly.

Additional multiple collision chemiluminescent studies to characterize ultrafast E-E transfer are underway for the YO and SiO molecules. Here pronounced effects are observed in both systems for several excited state levels. Similar studies might also be instituted on the tin oxide system to check certain observations made by Fontijn and Felder, namely, are there specific levels of the $a^3\Sigma^+$ state to which energy transfer is very efficient? If so, how can this be used to improve the efficiency of a potential tin oxide laser system?

It is also of interest to obtain and/or develop appropriate theoretical models to explain ultrafast energy transfer. As a result of my attending the Gordon Conference on Energy Transfer, several models are now under consideration to explain the magnitude of the effects which we have observed. At present, we have demonstrated that the observed energy transfer in BO cannot be related to $A^2\Pi - X^2\Sigma^+$ overlap factors.

c. "Selective Chemical Reactions"

We have continued our studies of the selective Group IIIB (Sc,Y) + Halogen reactions, finding that quenching of selectively populated excited states is significant for product metal chlorides, bromides, and iodides but not the metal fluorides. Therefore, we are focusing on the fluoride systems ($Sc + F_2$, $Y + F_2$) in studying reactions of potential use in a laser cavity.

In addition to our experimental effort, we are also working on the theory for these systems within the electron jump framework. Here we are hoping to work out some collaboration with Professor Bates and his group in Belfast. Professor Bates and his colleagues have worked on the most detailed theories for the modeling of charge transfer processes. We have communicated our chemiluminescent results to him. Finally, we should note that there is some question about the possible contribution of metal dimer-halogen atom reactions to the selective metal monohalide emission now associated with Group IIIB metal atom-halogen molecule reaction. In order to investigate this possibility, we have constructed a device to carry out halogen *atom* metatheses.

d. "Construction of a New Laser Cavity"

We should note that Mr. Winfred Crumley has been working on a new laser cavity design which we hope to augment in the next six to eight weeks. The flow patterns in this system are first being modeled with a large plexi-glass-water system.

e. "Future Possibilities"

We feel that the program which we have initiated in these six months has greatly benefitted the Bell-Aerospace effort and the Army chemical laser effort in general. Clearly, the previous discussion points to many areas where future research effort is strongly needed. It is clear that much of this overall effort could not be brought to completion in the present six month period. In addition, the Bell-Aerospace group does need further continued support in their efforts. An example of further support involving efforts not mentioned above would involve the construction of intercavity "laser gain" studies to assess the gain of the (0,2), (0,3), and (0,4) SnO $a^3\Sigma^+ - X^1\Sigma^+$ transitions. This can be accomplished with a Rhodamine 6G continuous wave dye laser currently available in our laboratory.

Personnel:

Personnel working on and at least partially supported by this project include Mr. Jeffrey Schmidt, Mr. Winfred Crumley, Ms. Beatriz Cardelino, and Dr. David Dever. In addition the principal investigator was partially supported by this contract. Mr. Bengt Ohlsson, Mr. Timothy Alborn, and Mr. William Pilcher also participated in the project and the materials and services necessary for their efforts were supported by the contract.

References:

1. W. Felder and A. Fontijn, J. Chem. Phys. 69, 1112 (1978).

2. A. Fontijn, "Kinetic Spectroscopy of Metal Atom/Oxidizer Chemiluminescent Reactions for Laser Applications", AeroChem Report TP-388.

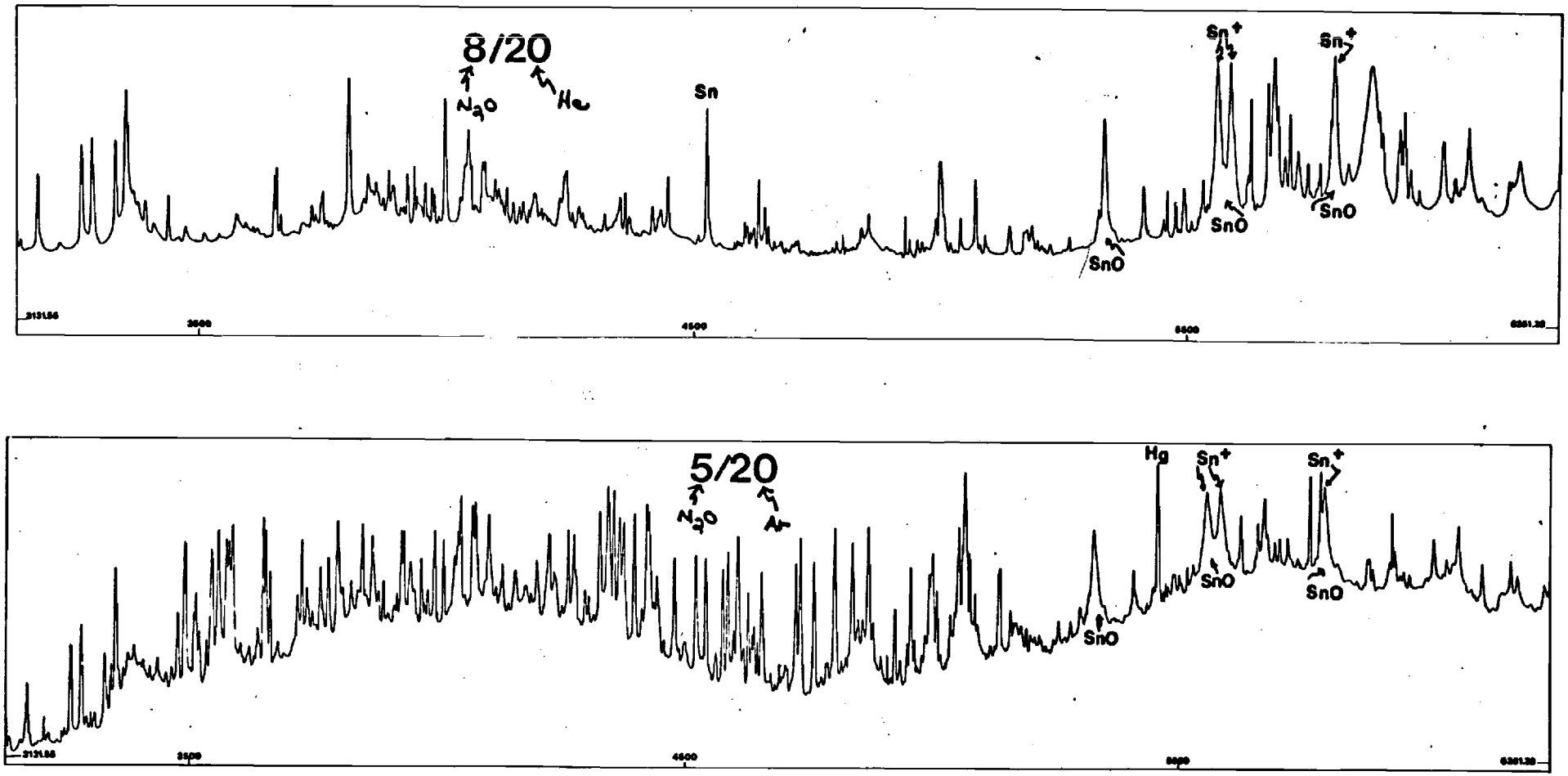


Figure 1

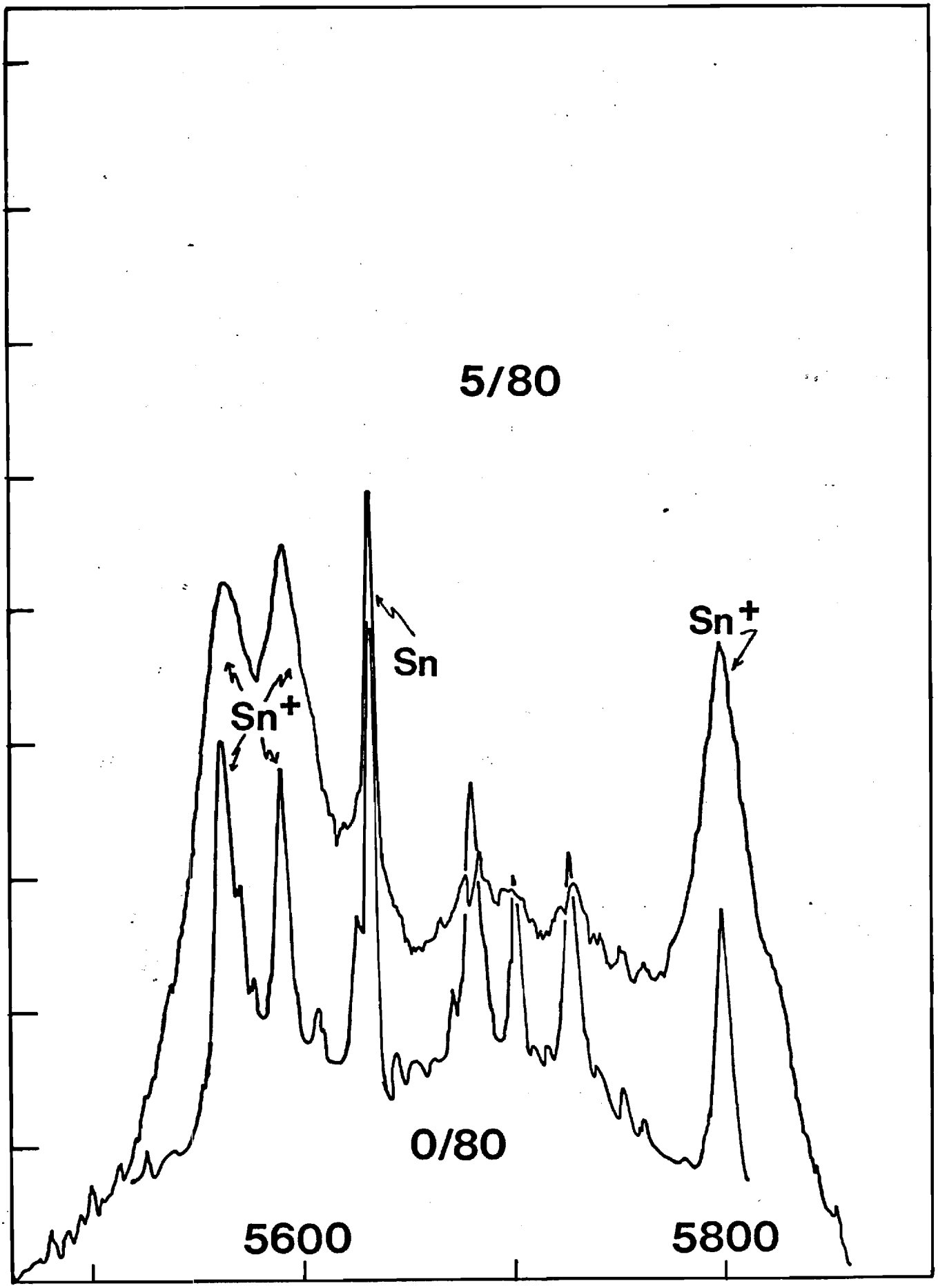


Figure 2

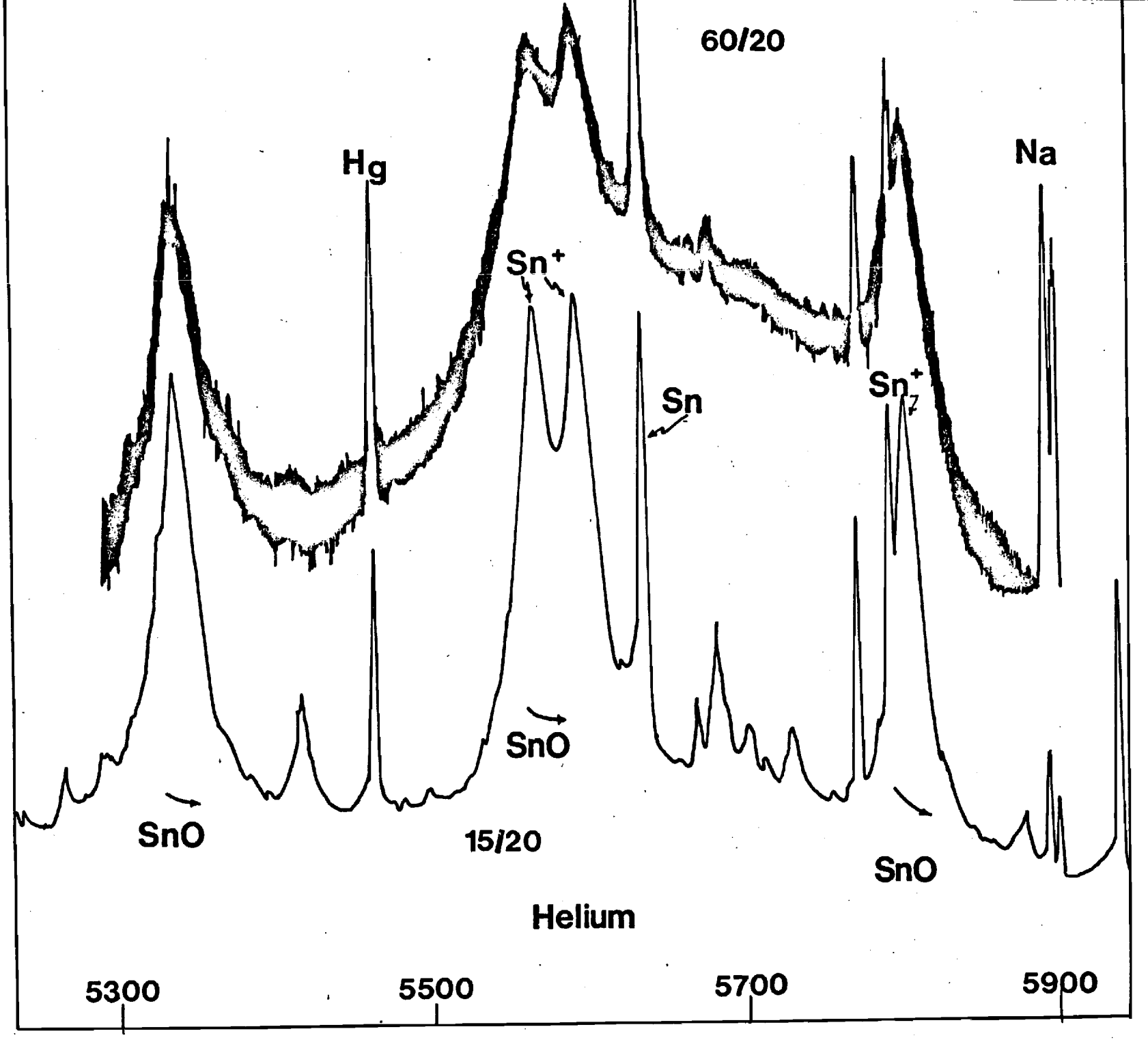
60/20
Hg
Na
Sn+
Sn
Sn+2
SnO
SnO
SnO
15/20
Helium
5300
5500
5700
5900

Figure 3

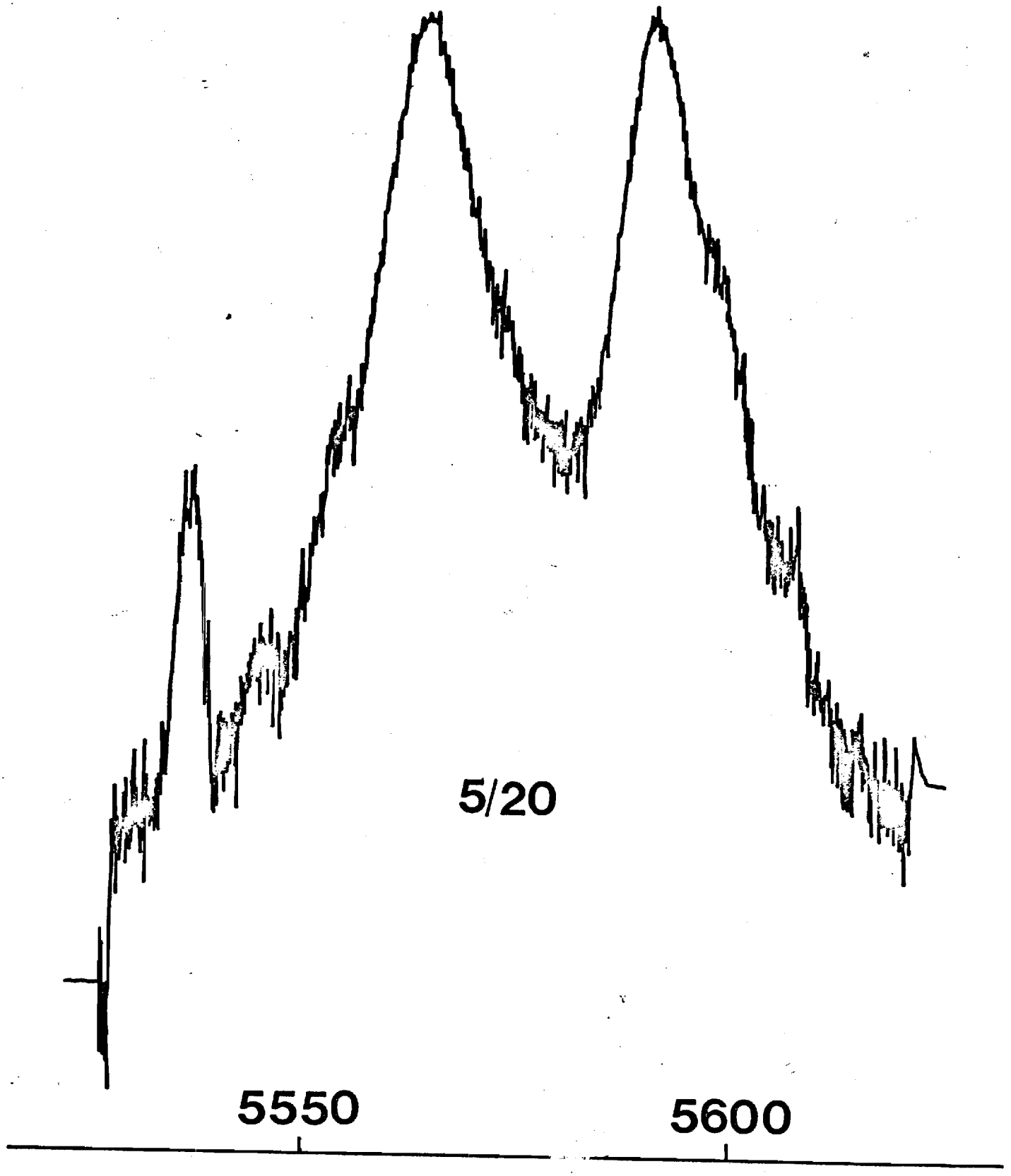


Figure 4(a)

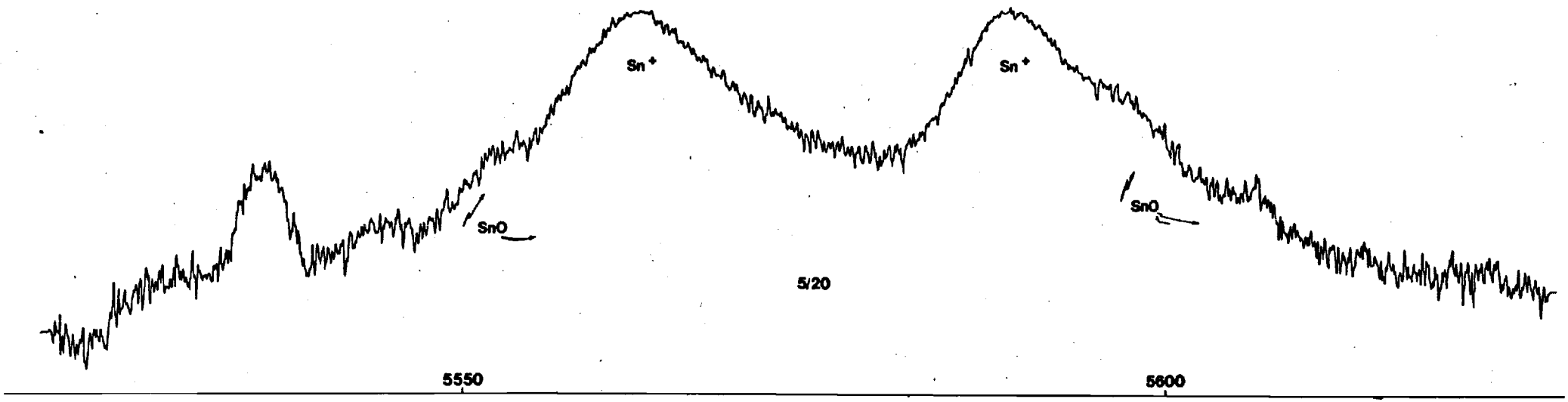


Figure 4(b)

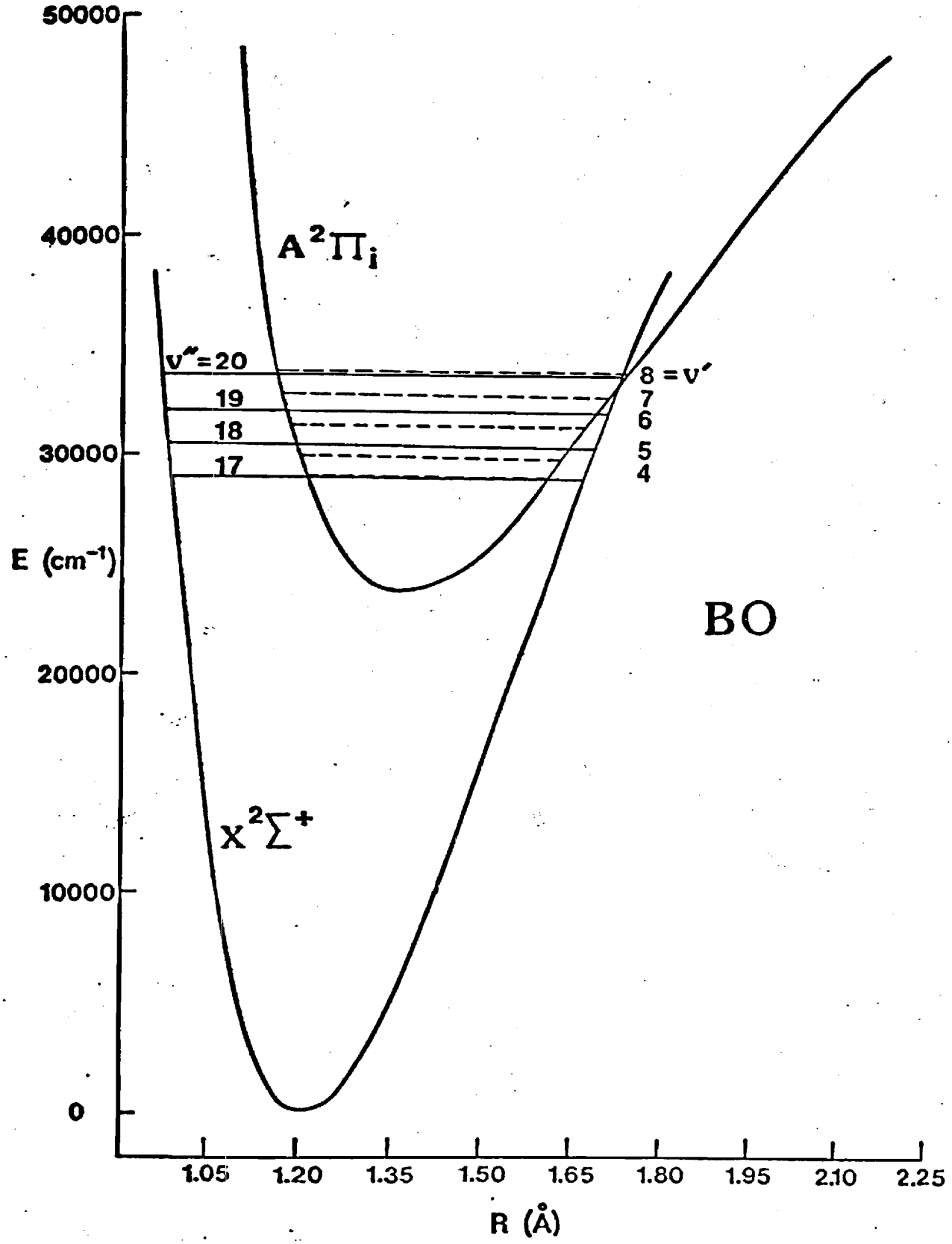
50000
40000
30000
20000
10000
0
E (cm⁻¹)
A²Π_i
X²Σ⁺
v''=20
19
18
17
8 = v'
7
6
5
4
BO
1.05
1.20
1.35
1.50
1.65
1.80
1.95
2.10
2.25
R (Å)

Figure 5

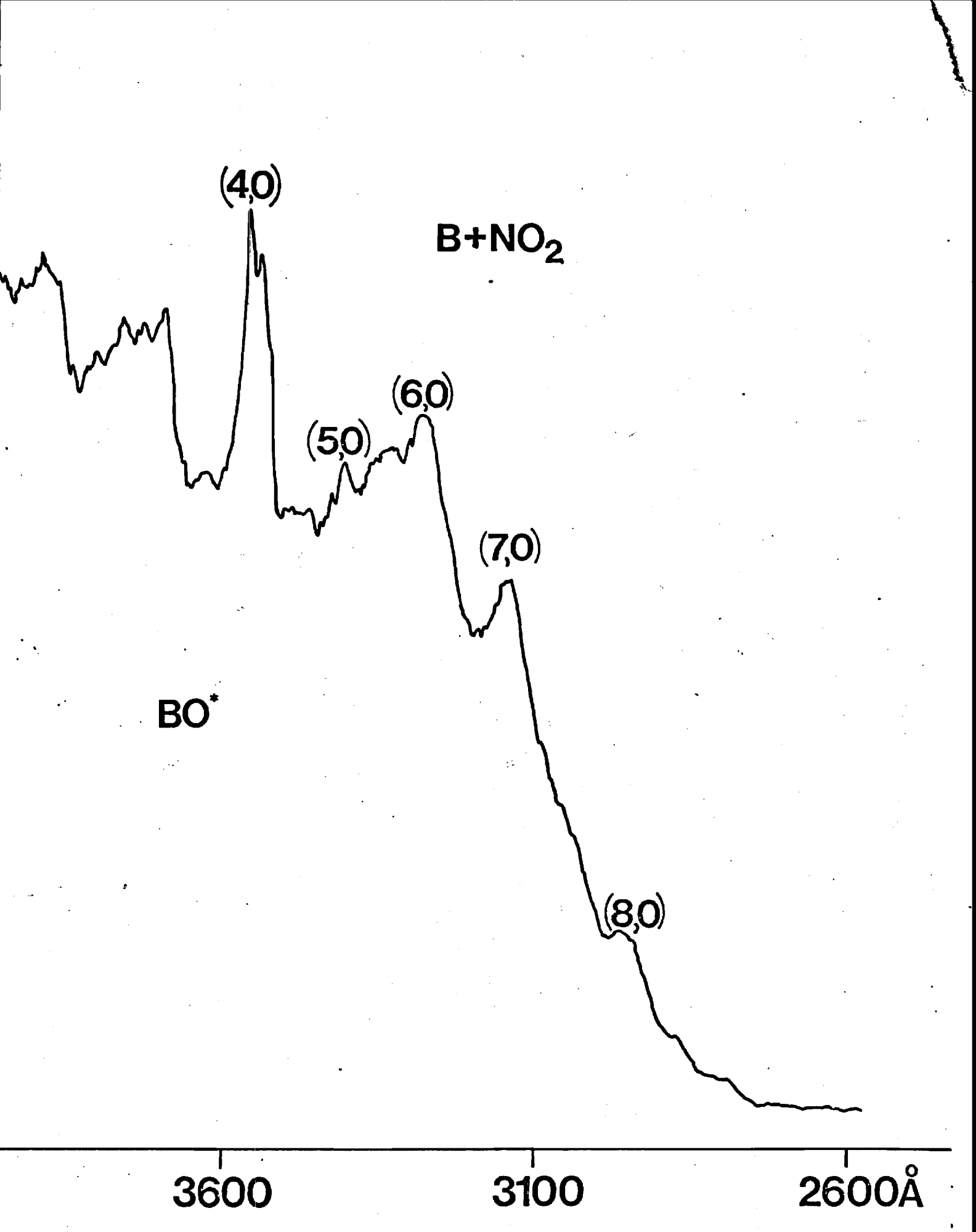


Figure 6(a)

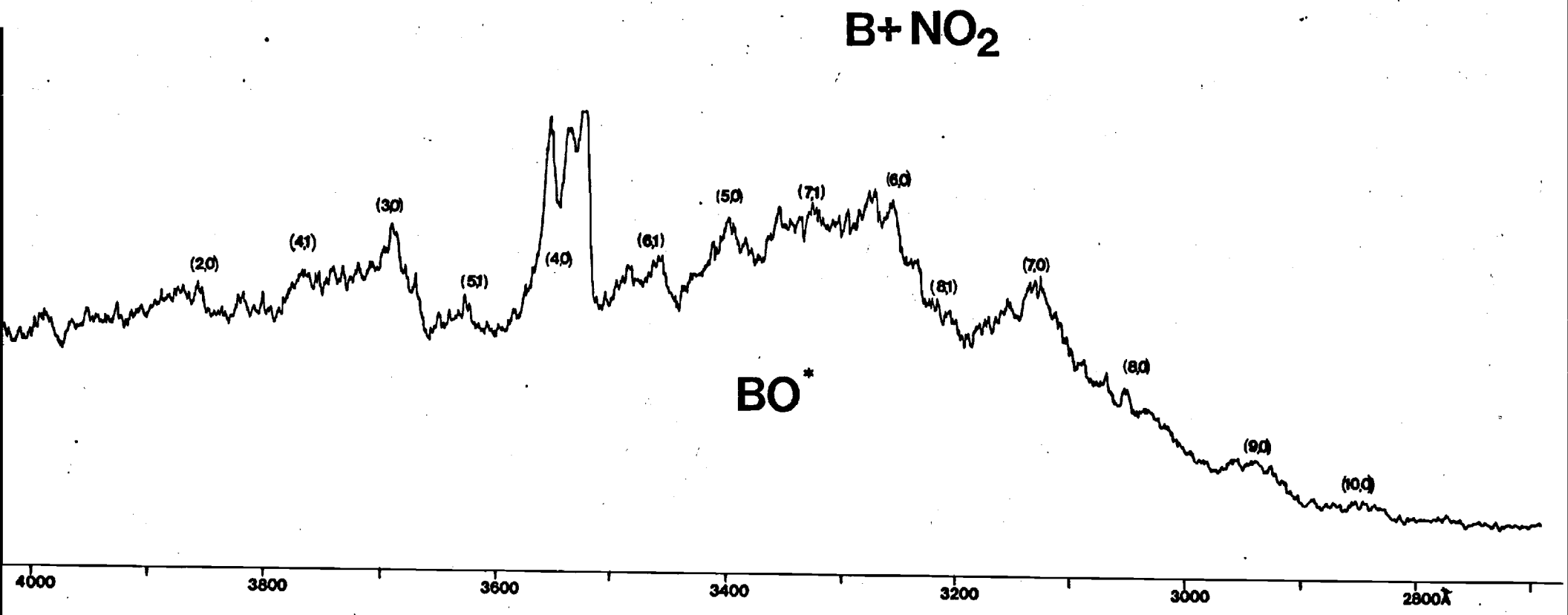
B+NO2
BO*
(2,0)
(4,1)
(3,0)
(5,1)
(4,0)
(6,1)
(5,0)
(7,1)
(6,0)
(8,1)
(7,0)
(8,0)
(9,0)
(10,0)
4000
3800
3600
3400
3200
3000
2800Å

Figure 6(b)

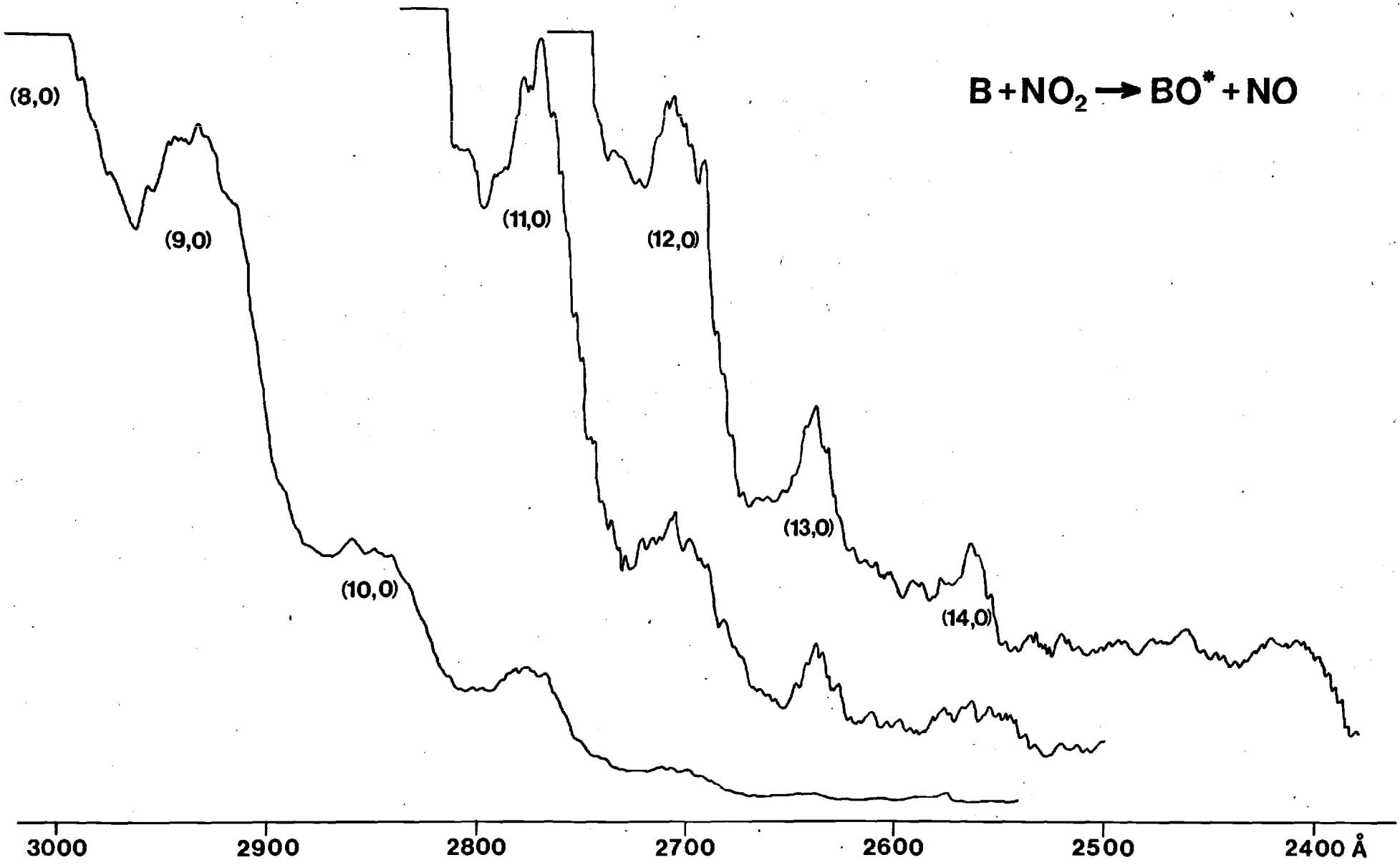
B + NO2 → BO* + NO
(8,0)
(9,0)
(10,0)
(11,0)
(12,0)
(13,0)
(14,0)
3000
2900
2800
2700
2600
2500
2400 Å

Figure 7